

CLAIMS as originally filed in the PCT application

1. Process for the preparation of a low-viscosity (poly)isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers, characterized in that the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of at least 50°C and of not more than 200°C for a period of not more than 24 hours.
2. Process according to Claim 1, characterized in that the starting reaction medium is heated to a temperature of at least 80°C, preferably of at least 120°C, and of not more than 170°C.
3. Process according to Claim 1 or 2, characterized in that the reaction medium is heated along a decreasing temperature gradient.
4. Process according to any one of the preceding claims, characterized in that the heating time is at least 5 minutes, preferably at least 30 minutes, and not more than 24 hours, preferably not more than 5 hours.
5. Process according to any one of the preceding claims, characterized in that at the end of the dimerization reaction, the starting monomer is removed, in particular by distillation.
6. Process according to any one of Claims 1 to 4 for the continuous preparation of a composition containing at least one isocyanate dimer containing a uretidinedione unit, characterized in that after the dimerization reaction, the unreacted monomers are removed and are recycled into the dimerization step.
7. Process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers, and optionally from other monomers,

this process comprising the following steps:

i) the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of at least 50°C, advantageously of at least 80°C, preferably of at least 120°C, and of not more than 200°C, advantageously of not more than 170°C, for a period of less than 24 hours, advantageously of less than 5 hours;

ii) the reaction mixture from step i) containing unreacted monomers is reacted with a (cyclo)trimerization or (cyclo)condensation catalyst, under (cyclo)trimerization or (cyclo)condensation conditions;

iii) the unreacted starting monomers are removed from the reaction mixture from step ii);

iv) the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer is isolated.

8. Process for the preparation of a low-viscosity polyfunctional isocyanate composition containing at least one isocyanate trimer containing an isocyanurate and/or biuret unit and at least one isocyanate dimer containing a uretidinedione unit, from starting isocyanate monomers, and optionally from other monomers, this process comprising the following steps:

i) the starting monomers are reacted with a (cyclo)trimerization or (cyclo)condensation catalyst under (cyclo)trimerization or (cyclo)condensation conditions;

ii) the reaction mixture from step i) containing unreacted isocyanate monomers is heated, in the absence of dimerization catalyst, to a temperature of at least 50°C, advantageously of at least 80°C, preferably of at least 120°C, and of not more than 200°C, advantageously of not more than 170°C, for a period of less than 24 hours, advantageously of less than 5 hours;

iii) the unreacted starting monomers are removed from the reaction mixture from step ii);

iv) the low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate trimer and at least one isocyanate dimer is isolated.

9. Process for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound having a function derived from the isocyanate function, starting with isocyanate monomers and another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:

i) the starting reaction medium is heated, in the absence of dimerization catalyst, to a temperature of greater than at least 80°C, advantageously at least 120°C, preferably at least 130°C, and less than at least 200°C, advantageously at least 170°C, for a period of less than 24 hours, advantageously less than 5 hours;

ii) the reaction product from step i) containing unreacted isocyanate monomers and a compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are reacted together, optionally in the presence of a catalyst;

iii) the isocyanate monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are removed from the reaction product from step ii);

iv) the polyfunctional isocyanate composition of low-viscosity comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other function derived from the isocyanate function, is isolated.

10. Process for the preparation of a low-viscosity polyisocyanate composition comprising at least one isocyanate dimer containing a uretidinedione unit and at least one other compound containing a function derived

from the isocyanate function, starting with isocyanate monomers and with another compound comprising at least one function other than isocyanate, which is reactive with the isocyanate function, this process comprising the following steps:

i) an isocyanate monomer is reacted with a compound comprising at least one function other than an isocyanate function, which is reactive with the isocyanate function, optionally in the presence of a catalyst;

ii) the reaction mixture from step i) containing unreacted isocyanate monomers is heated, in the absence of dimerization catalyst, to a temperature of greater than at least 80°C, advantageously at least 120°C, preferably at least 130°C and not more than 200°C, advantageously not more than 170°C, for a period of less than 24 hours, advantageously less than 5 hours;

iii) the monomers and, where appropriate, the compound comprising at least one function other than the isocyanate function, which is reactive with the isocyanate function, are removed from the reaction mixture from step ii);

iv) the low-viscosity polyisocyanate composition comprising at least one polyisocyanate trimer and at least one polyisocyanate dimer is isolated.

11. Process according to any one of Claims 7 to 10, characterized in that the isocyanate dimer is obtained by heating the reaction medium along a decreasing temperature gradient.

12. Process according to Claim 9 or 10, characterized in that the function derived from the isocyanate function is a carbamate, allophanate, urea, biuret and/or masked isocyanate function.

13. Process according to Claim 9 for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function, comprising the reaction, in step ii), of isocyanat

monomers with water.

14. Process according to Claim 10 for the preparation of a low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer, and at least one compound having a biuret function, comprising the reaction, in step i), of isocyanate monomers with water.

15. Process according to any one of the preceding claims, characterized in that, for the dimerization of the starting monomers, a compound of general formula I:

in which

R is a mono- or n-valent hydrocarbon-based group having from 1 to 30 carbon atoms, in which the hydrocarbon-based chain can be interrupted by one or more chalcogen atoms and can bear 1 to 3 OH groups, and n is an integer ranging from 1 to 3,

and/or products derived from this derivative by a reaction with a compound bearing an aliphatic isocyanate function,

is added to the reaction medium containing the starting monomers.

16. Process according to Claim 15, characterized in that the said products derived from the reaction of the compound of general formula I with a compound bearing an aliphatic isocyanate function correspond to the general formulae II and/or III below:

in which

one or more of X_1 , X_2 and X_3 represents a group $R'(-N=C=O)_p$ in which R' is a p-valent aliphatic group and p is an integer ranging from 0 to 5, the others representing, where appropriate, a group of formula

R' and p being as defined above,

R_1 is R , with the OH groups substituted, where appropriate, with a group $CONX_1H$, X_1 being as defined above,

at least one of $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ represents the group

R' and p being as defined above, the others representing a group NX_1H or NX_1 -silyl with X_1 as defined above and R_2 being R , with the OH groups substituted, where appropriate, with a group $CONX_1H$, or

R' and p being as defined above, and

n is an integer ranging from 1 to 3.

17. Process according to Claim 15 or Claim 16, characterized in that R is a C_1 - C_4 alkyl group substituted with 1 to 3 OH groups.

18. Process according to any one of Claims 15 to 17, characterized in that the compound of general formula I is chosen from pentaerythritol and trimethylolpropane,

and the compounds of general formulae II and III are chosen, where appropriate, from the corresponding pentaerythritol and trimethylolpropane derivatives as defined in Claim 16.

19. Process according to any one of the preceding claims, characterized in that the starting isocyanate monomers are diisocyanates chosen from hexamethylene diisocyanate, tetramethylene diisocyanate, norbornane dimethylene diisocyanate, isophorone diisocyanate, bis(isocyanato)cyclohexylmethane and 2-methylpentamethylene diisocyanate.

20. Use of a compound of general formula I:

in which

R is a mono- or n-valent hydrocarbon-based group having from 1 to 30 carbon atoms, in which the hydrocarbon-based chain can be interrupted by one or more chalcogen atoms and can bear 1 to 3 OH groups, and n is an integer ranging from 1 to 3,

and/or products derived from this derivative by reaction with a compound bearing an aliphatic isocyanate function,

for the preparation of isocyanate dimers from aliphatic isocyanate monomers, with a degree of conversion of at least 5%, preferably at least 10%, of the starting isocyanate functions into uretidinedione functions.

21. Use according to Claim 20, characterized in that the said products derived from the reaction of the compound of general formula I with a compound bearing an aliphatic isocyanate function correspond to the general formulae II and/or III below:

in which

one or more of X_1 , X_2 and X_3 represents a group $R'-(N=C=O)_p$, in which R' is a p -valent aliphatic group and p is an integer ranging from 0 to 5, the others representing, where appropriate, a group of formula

R' and p being as defined above,

R_1 is R , with the OH groups substituted, where appropriate, with a group $CONX_1H$, X_1 being as defined above,

at least one of $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ represents the group

R' and p being as defined above, the others representing a group NX_1H or NX_1 -silyl with X_1 as defined above and R_2 being R , with the OH groups substituted, where appropriate, with a group $CONX_1H$, or

R' and p being as defined above, and
n is an integer ranging from 1 to 3,
for the preparation of dimeric compounds of general
formula X:

in which R' and p are as defined in Claim 20, starting
with isocyanate monomers of general formula VII:



R' and p being as defined above, with a degree of
conversion of advantageously 5%, preferably 10% at least
of the isocyanate functions into compounds of formula X.

22. Use according to Claim 20 or Claim 21,
characterized in that R is a C₁-C₄ alkyl group
substituted with 1 to 3 OH groups.

23. Use according to Claim 21, characterized in that
the compound of general formula I is chosen from penta-
erythritol and trimethylolpropane, and the compounds of
general formulae II and III are chosen, where
appropriate, from the corresponding pentaerythritol and
trimethylolpropane derivatives as defined in Claim 21.

24. Use according to Claim 21, characterized in that
the reaction for the preparation of the compounds of
general formula X from the compounds of general formula
VII is carried out in a reaction medium also comprising
compounds of general formula VIII:

in which R' and p are as defined in Claim 21.

25. Use according to Claim 21, characterized in that the compound of general formula I, and/or III and/or III is bound to a support, in particular a resin.

26. Low-viscosity polyfunctional isocyanate composition comprising at least one uretidinedione isocyanate dimer and at least one compound having a biuret function.

27. Low-viscosity polyfunctional isocyanate composition according to Claim 26, comprising at least 3%, advantageously at least 10%, preferably at least 20%, by weight of compounds containing a biuret unit.

28. Composition comprising at least one compound of general formula X:

in which R' and p are as defined in Claim 21,
and at least one compound of general formula II:

in which one or more of X₁, X₂ and X₃ represents a group -R'-N=C=O as defined above and the others represent, where appropriate, a group

R' and p being as defined above,
and R₁ is R, with the OH groups substituted, where appropriate, with a group CONX₁H as defined above,

and n being an integer from 1 to 3;
and/or at least one compound of general formula III:

in which at least one of $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$,
represents the group

R' and p being as defined above, the others representing
a group NX_1H with X_1 as defined above, and
 R_2 being R, with the OH groups substituted with a group
 $CONX_1H$ or

as defined above,
and n is an integer ranging from 1 to 3,
and/or a biuret compound obtained from an isocyanate of
general formula VI as defined in Claim 21, the said
composition also being characterized in that it is free
of dimerization catalyst of phosphine, aminopyridine,
phosphoramidate, organometallic or tertiary amine type.

29. Composition according to Claim 28, characterized
in that it also comprises a compound of general formula
VIII:

R' and p being as defined in Claim 21
and/or a compound of general formula XIII

in which R'' represents H or a hydrocarbon-based group
and R' and p are as defined above.

30. Composition comprising at least one compound of
general formula X as defined in Claim 28 and/or
optionally one compound of general formula VIII as
defined in Claim 29 and/or at least one compound of
general formula XIII as defined in Claim 24, the said
composition being free of dimerization catalysts.

31. Compound of general formula III as defined in
Claim 16, in which at least one of the groups $NX'_1X''_1$,
 $NX'_2X''_2$ and $NX'_3X''_3$, represents the group of formula V as
defined above, the others representing a group NX_1H with
 X_1 , $X'_1X''_1$, $X'_2X''_2$ and $X'_3X''_3$, as defined in Claim 16 and
 R^1 as defined in Claim 16, i.e. representing a group R
with the OH groups substituted, where appropriate, with
a group $CO-NX_1H$ or a group of formula V, as defined in
Claim 16.

32. Compound of general formula III in which

- the groups $NX'_1X''_1$, $NX'_2X''_2$ and $NX'_3X''_3$ are
chosen from a group of general formula NX_1H , a group of
general formula V as defined above, a uretidinedione
group of formula IV, an isocyanurate group of formula XI

R' and p being as defined in Claim 16, a biuret group of

formula XII

R' and p being as defined in Claim 16,

R'' represents H or a hydrocarbon-based group,

R₂ represents the group R with the OH groups substituted, where appropriate, with a group chosen from CONHX₁H, a group of formula VI, a group of formula VI, a group of formula -CO-NH-(group of formula IV), -CO-NH-(group of formula XI) and -CO-NH-(group of formula XII), with the proviso that the compounds containing at least one carbamate group of formula NX₁H, or CONHX₁H respectively, and/or allophanate group of formula V, or -CO-NH-(group of formula V) respectively, and at least one group chosen from a uretidinedione group of general formula IV, or -CO-NH-(group of general formula IV), respectively, an isocyanurate group of general formula XI, or -CO-NH-(group of general formula XI) respectively, and a biuret group of general formula XII, or -CO-NH-(group of general formula XII) respectively.

33. Compounds according to Claim 31 or Claim 32, in which p is equal to 1 and containing 1, 2, 3 or 4 allophanate groups.

34. Compounds according to Claim 31 or Claim 32, characterized in that R' is a group chosen from a group (CH₂)_n with n ranging from 2 to 8, optionally substituted with a hydrocarbon-based chain optionally bearing an isocyanate function, a norbornylmethylene group, a cyclohexylmethylene group or a 3,3,5-trimethylcyclohexylmethylene group.

35. Use of a composition according to Claim 28 or Claim 29, for the preparation of a polyurethane coating.

36. Composition for simultaneous or successive application, comprising:

- at least one polyisocyanate composition

according to one of Claims 26 to 30, and

- a polyol.

37. Composition according to Claim 36, characterized in that the polyol is a polyol of acrylate type which satisfies the following conditions for a dry extract (DE) of 75-80%, by weight:

- Mw (weight-average molecular weight) not greater than 10,000, advantageously not greater than 5000, preferably not greater than 2000;

- Mn (number-average molecular weight) of not greater than 5000, advantageously not greater than 3000, preferably not greater than 800;

- Mw/Mn (dispersity ratio) of not greater than 5, advantageously not greater than 3, preferably not greater than 2;

- number of OHs/molecule of greater than or equal to 2, advantageously greater than 2.

38. Composition according to Claim 36, characterized in that the polyol is a polyol of polyester type having 100% dry extract and a viscosity of not greater than 10,000 mPa.s, advantageously not greater than 5000 mPa.s, preferably not greater than 1000 mPa.s, and an Mw of between 250 and 8000.

39. Composition according to one of Claims 36 to 38, containing a crosslinking catalyst, which is optionally a latent catalyst.